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HOW GOOD ARE AMBIENT AIR POLLUTION MEASUREMENTS?

by

Raymond C. Rhodes and E. Gardner Evans
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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Raymond C. Rhodes
Quality Assurance Specialist
Environmental Protection Agency
Research Triangle Park, NC 27711

E. Gardner Evans
Operations Research Analyst
Environmental Protection Agency
Research Triangle Park, NC 27711

ABSTRACT

In accordance with Federal regulations, state and local air pollution control agencies have, since January 1, 1981, been performing special checks of their ambient air measurement systems to assess the precision and accuracy of the monitoring data. The measurement methods involved are those for total suspended particulate, nitrogen dioxide, sulfur dioxide, carbon monoxide, ozone, and lead. The precisions of the measurement systems are estimated by some type of replicate measurement, including the use of collocated samplers. Accuracies of the measurement systems are estimated by measurement of, or comparison with, reference materials or devices. Because the variations of imprecision and inaccuracy are usually proportional to pollution concentration levels the assessments are expressed on a percentage basis. The precision and accuracy assessments are reported to EPA. Annual EPA reports are issued to summarize and evaluate the data quality. Appreciable variation of data quality exists across the regions, states, and local agencies of the nation. Since 1981, some improvement in data quality has been evidenced. Whenever data users request monitoring data from the National Aerometric Data Bank, the users automatically receive precision and accuracy assessments of the corresponding air monitoring agencies. Planned revisions to the reporting procedure will require that the precision and accuracy assessments will be identified to each individual monitoring site.

INTRODUCTION

Ambient air pollution measurements have been made for many years by state and local air pollution monitoring agencies. With the establishment of the federal Environmental Protection Agency (EPA) in 1972 and the subsequent establishment of national ambient air quality standards the number of air pollution measurements made by the state and local agencies to monitor the quality of the air have increased considerably. Measurements of the air pollutants for which standards exist (the so-called criteria pollutants) have since 1972 been supplied to EPA's National Aerometric Data Bank (NADEB) in Durham, NC. These data are used by EPA to track long-term trends in air quality as a measure of the effectiveness of the air pollution control activities and to develop control strategies for the nation.

Although EPA had developed and issued a number of guidance documents recommending quality assurance practices, each state and local agency planned and implemented their own quality assurance programs. However, in 1979 EPA issued regulations which required the quality assurance programs of the states to meet certain minimum requirements. The regulations also required that the states perform specified internal-but-independent checks to assess the precision and accuracy of the pollutant measurement systems and to report the results to EPA. The results of the special checks are immediately useful to the monitoring agencies as supplementary data for internal quality control purposes. EPA summarizes and evaluates the precision and accuracy assessments on regional and national bases. The system for summarizing and evaluating the results is called the Precision and Accuracy Reporting System (PARS).

To provide a comparison of pollutant concentration levels used in the audit program with the concentrations specified in the National Ambient Air Quality Standards (NAAQS), the standards for the criteria pollutants are currently:

<u>Pollutant</u>	<u>Primary Standard, $\mu\text{g}/\text{m}^3$ (ppm)</u>
Total Suspended Particulate (TSP)	
Annual Average	75
24-hour Average	260
Sulfur Dioxide (SO_2)	
Annual Average	80 (0.030)
24-hour Average	365 (0.139)
Nitrogen Dioxide (NO_2)	
Annual Average	100 (0.053)
Carbon Monoxide (CO)	
8-hour Average	10,000 (8.7)
1-hour Average	40,000 (34.8)
Ozone (O_3)	
1-hour Average	240 (0.122)
Lead (Pb)	
Quarterly Average	1.5

TEXT

Precision and Accuracy Reporting System (PARS) The federal regulations require that the states or subordinate districts within the states perform certain specified checks to assess the precision and accuracy of their measurement systems. The precision checks are duplicate or repeated measurements made at ambient concentration levels.

TABLE I. REQUIREMENTS FOR PERFORMING PRECISION CHECKS

<u>Parameter</u>	<u>Precision Check Level</u>	<u>Frequency</u>
CO (continuous analyzer)	8 - 10 ppm	Once each 2 weeks
SO ₂ , NO ₂ , and O ₃ (continuous analyzers)	0.08 - 0.10 ppm	Once each 2 weeks
TSP, SO ₂ , and NO ₂ (manual methods)	Ambient Concentrations (Collocated Samplers)	Once each 6 days
Pb (manual methods)	Ambient Concentrations (Duplicate Filter Strips)	Once each 6 days

The accuracy checks are internal-but-independent accuracy audits made at specified concentration or flow levels. The audits of continuous analyzers are performed by challenging the analyzers with independently prepared "calibration" gases traceable to the National Bureau of Standards (NBS). The audits of the manual methods check the accuracy of only a portion of the total measurement method. For TSP, only the flow measurement portion is audited. For the SO₂ and NO₂ methods, only the analytical portion is audited. For Pb, the analytical portion is audited directly; however, the sampling is obtained by use of the TSP sampler, and thus, assessments of both the flow and analytical portions of the method are available.

TABLE II. CONCENTRATION LEVELS FOR CONDUCTING ACCURACY AUDITS

Method		Level 1	Level 2	Level 3	Level 4
Continuous SO ₂ , NO ₂ , and O ₃	(ppm)	.03 - .08	.15 - .20	.35 - .45	.80 - .90
Continuous CO	(ppm)	3 - 8	15 - 20	35 - 45	80 - 90
TSP, flow	(m ³ /min.)		1.13 - 1.70		
Manual SO ₂ *	(ppm)	.013 - .020	.033 - .040	.053 - .059	
Manual NO ₂ *	(ppm)	.018 - .028	.046 - .055	.074 - .083	
Manual Pb**	(ug/m ³)	.6 - 1.8	3.5 - 5.9		

* Concentration levels corresponding to flow rates of .2 L/min.

** Concentration levels corresponding to flow rates of 50 cfm.

The results of the precision and accuracy checks are expressed as percentage deviations of the observed values from the expected, or "known", values. Each state or subordinate district summarizes the results of their checks each calendar quarter and reports the results as 95 percent probability limits:

$$\bar{D} \pm 1.96 S$$

where $\bar{D}$ = the average of the percent differences

S = the standard deviation of the individual percent differences

1.96 = the standard deviate value corresponding to 95 percent probability, assuming a normal distribution

The standard deviation, S, of the percent differences is effectively the coefficient of variation for the measurement method at the concentration level involved. For precision, the standard deviation (or coefficient of variation) represents the within-instrument variability for the continuous and manual methods. For accuracy, the standard deviation (or coefficient of variation) represents the between-instrument variability (or biases) for continuous methods, and the within-laboratory variability of the particular portion of the manual method checked.

The audit results presented in this report are the average coefficients of variation of all the agencies in the nation. Obviously, about half of the agencies are better than the average and about half are worse.

Precision. The precisions of the various measurement methods, expressed as coefficients of variation (CV), are:

Manual Methods		Continuous Methods	
Pollutant	CV, %	Pollutant	CV, %
SO ₂	20.4	SO ₂	5.9
NO ₂	16.1	NO ₂	6.6
TSP	6.4	O ₃	4.8
Pb	7.9	CO	4.1

The variabilities of the manual methods are larger than for the continuous methods. However, these comparisons are not strictly valid because the precision checks for the continuous methods are made at the specified concentration levels (Table I) whereas the precisions of the manual methods are obtained from the results of collocated samplers (duplicate filter strips for Pb) at various ambient concentrations. More valid comparisons could be made for the SO₂ and NO₂ methods if the results from the collocated samplers were obtained at the same concentrations as those for the continuous methods. Nevertheless, the magnitude of the variation for the manual SO₂ and NO₂ methods are appreciable and provide justification to change to the continuous, but more expensive, methods.

Accuracy, Manual Methods. Figure 1 presents the accuracy results for the manual methods. The coefficient of variation for accuracy represents the variability of the accuracy audit results across the monitoring agencies in the nation. The average of all the agencies was very close to zero, as should be expected or hoped. And as expected, the variabilities of the accuracy audit results, expressed in percentage form, are larger at low concentration levels.

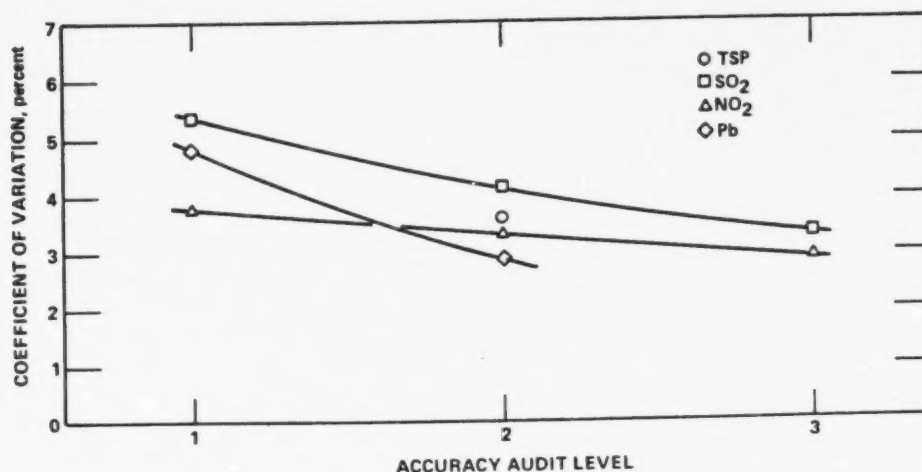


Figure 1. Accuracy Coefficients of Variation, Manual Methods

Components of Variability, Manual Methods. The accuracies of the manual methods are reasonably small. However, it is emphasized that only a portion of the total measurement system is being checked. The true accuracies of the manual methods cannot be any better than the precisions. Under the optimum but unrealistic assumption that the inaccuracies are the result of imprecision only, it is interesting to compute the extent of variability which is unexplained by the accuracy audit results. Under the above assumption, the following relationship exists:

$$(CV)_{\text{precision}}^2 = (CV)_{\text{accuracy}}^2 + (CV)_{\text{unexplained}}^2$$

The following table presents the computed coefficients of variation unexplained by the accuracy audit results:

Manual Method	Precision, CV %	Accuracy, CV % (Level 1)	Unexplained Variation, CV
TSP	6.4	3.5 (flow)	5.4
SO ₂	20.4	5.5 (analytical)	19.6
NO ₂	16.1	3.8 (analytical)	15.6
Pb	7.9	4.8 (analytical)	6.3

The results for the TSP and NO₂ methods are presented in graphical form in Figures 2 and 3. Similar charts could be drawn for the Pb and SO₂ methods. The sources of variability which contribute to the unexplained variability include the following:

Method	Possible Sources of Variability Unexplained by Accuracy Audit Data
TSP	Filter weighing, before and after exposure Filter conditioning for weighing, before and after exposure Loss of particulate or fibers from filter after pre-weighing Collection of particulate
SO ₂ , NO ₂	Collection efficiency variation Loss of absorbing solution during sampling or in transport or handling prior to analysis Variation in flow rate measurement
Pb	Variation from strip-to-strip within a filter Loss of particulate in transport, handling, or cutting of strips Inaccurate cutting of filter strips

Because the manual SO₂ and NO₂ methods are being replaced by the continuous methods, it would probably not be worthwhile investigating the sources of variability for these methods. However, for the TSP and Pb methods, some studies should be pursued to determine the contribution of the various sources of variation with a goal of reducing the total variability.

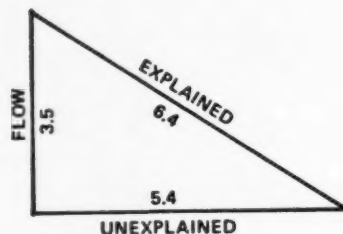


Figure 2. Explained and Unexplained Variability
TSP Method

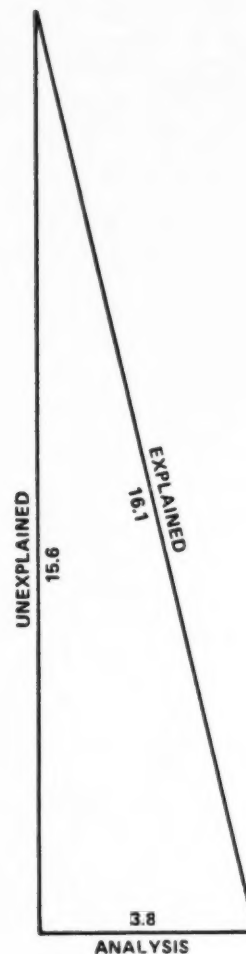


Figure 3. Explained and Unexplained Variability
Manual NO₂ Method

Because the Pb method involves the sampling method of the TSP method and a chemical analysis for Pb of the particulate collected, it is possible and of interest to combine the two separate estimates of variability. First, combining the accuracy audit results for the TSP flow audit (CV = 3.5%) and the accuracy audit results for the Pb analysis (CV = 4.8%) gives a resulting "total" coefficient of variability of 5.9%. See Figure 4.

$$\begin{aligned} (CV)_{\text{flow}}^2 + (CV)_{\text{analysis}}^2 &= (CV)_{\text{combined}}^2 \\ (3.5)^2 + (4.8)^2 &= (5.9)^2 \end{aligned}$$

However, it is noted that the 5.9% value is less than either the coefficient of variation for precision of the Pb analysis (CV = 7.9%), or that of the TSP method (CV = 6.4%) ! If it could be assumed that weighing portion of the TSP method is very small and can be assumed to be negligible, then the CV for the TSP precision includes the error variations of the flow rate, the variation in collection of the Pb particulate from sampler to sampler, and possible loss of particulate from the filters in handling, then it is considered appropriate to combine the two CV's to estimate the total imprecision of the Pb method:

$$\begin{aligned} (CV)_{\text{sampling}}^2 + (CV)_{\text{analysis}}^2 &= (CV)_{\text{combined}}^2 \\ (6.4)^2 + (7.9)^2 &= (10.2)^2 \end{aligned}$$

These variations are presented in Figure 5.

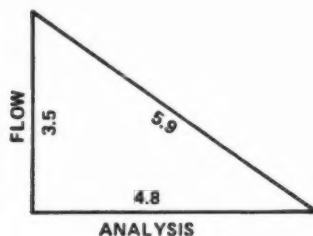


Figure 4. Combined Accuracy Variability
Pb Method

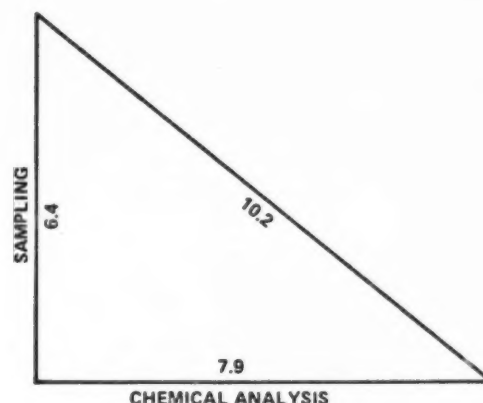


Figure 5. Combined Precision Variability
Pb Method

The CV of 10.2 % for imprecision is nearly twice the CV of 5.9 % for accuracy! This can be explained by the following factors:

1. The precision estimate for sampling is based on differences between real samples collected over a 24-hour period, whereas the accuracy estimate is based only on an audit check of the flow measurement only made at a point in time.
2. The precision estimate for the chemical analysis is based on differences between duplicate strips from real particulate filter samples, whereas the accuracy estimate is based only on an analysis of an unexposed filter strip to which a synthetically prepared solution containing Pb has been added.
3. The accuracy audits for both flow and chemical analysis may have been performed with more-than-routine care, whereas the routine flow measurements and particulate determinations for the collected TSP samples and the routine analysis of the duplicate filter strips were given only routine care.

For the above reasons, the combined CV for Pb (10.2 %) is probably a more correct estimate.

Accuracy, Continuous Methods. Figure 6 presents the results of the accuracy audits for the continuous methods. The results in terms of the coefficient of variability are plotted at the accuracy audit levels 1, 2, and 3. Note that the variabilities are higher at the lower concentrations, the same as for the manual methods, and that the variabilities tend to become constant at the higher levels. Also shown on the chart for comparison purposes are the precision results located at their approximate relative concentration level. Note that for CO, SO₂, and O₃ the values for precision fall closely in line with the curves for the accuracy results, indicating that practically all of the variability in accuracy is the result of imprecision. In other words, any errors of the calibration process are very small. Such is not the case however for the NO₂ method. As indicated on Figure 6, the expected variation of accuracy at the concentration level of the precision check is about 8.2 %, compared to 6.6 % for the precision variability.

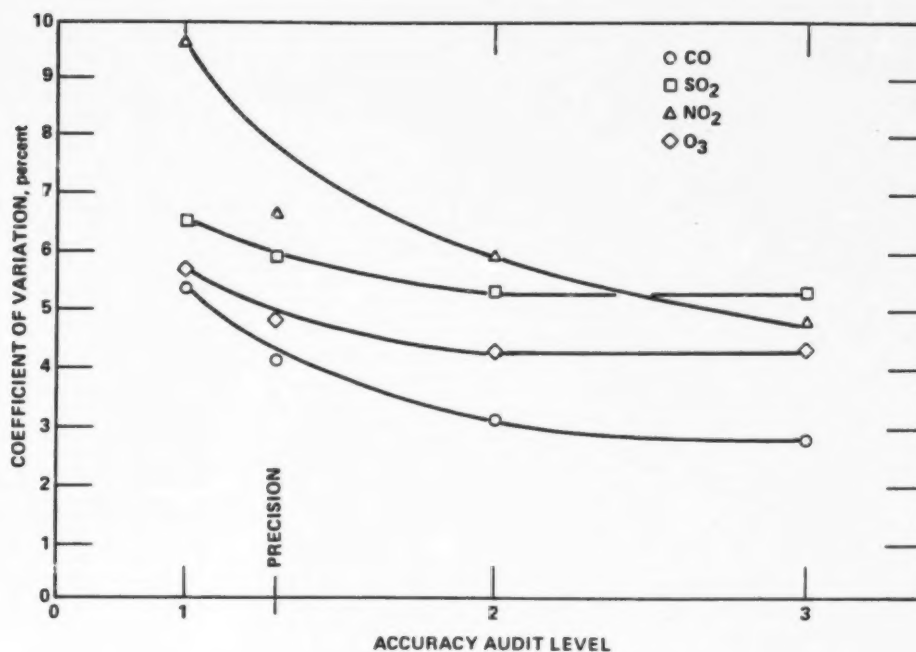


Figure 6. Accuracy Coefficients of Variation, Continuous Methods

Components of Variability, Continuous Methods. The following appropriate relationship can be used to estimate the variability of the accuracy results which are not explained by the variability of imprecision for the continuous NO₂ method:

$$\begin{aligned}
 (CV)_{\text{accuracy}}^2 &= (CV)_{\text{precision}}^2 + (CV)_{\text{unexplained}}^2 \\
 (8.2)^2 &= (6.6)^2 + (CV)_{\text{unexplained}}^2 \\
 (CV)_{\text{unexplained}}^2 &= 4.9
 \end{aligned}$$

Thus, an unexplained variability of 4.9 % may possibly be explained by variability in the calibration process. The calibration process for continuous NO₂ instruments is more complicated than for the CO, SO₂, and O₃ methods. It may be worthwhile investigating the NO₂ calibration process to determine more precisely the cause of the additional variability. Appropriate modification of the calibration process may reduce some of the variability

CONCLUSIONS

Evaluation of the results obtained from the special precision and accuracy assessments from the air pollution control agencies in the nation provides useful information concerning the inherent variabilities of the measurement methods in routine monitoring. The general pattern is that the variabilities on a percentage basis are larger at low concentrations but become essentially constant at higher levels. A study of the components of variability in the measurement systems indicates areas where further investigational work or tighter controls may be needed. At the local agency level, the precision and accuracy assessments provide supplementary data for local quality control uses.

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